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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : H01C 7/02	A1	(11) International Publication Number: WO 90/03651 (43) International Publication Date: 5 April 1990 (05.04.90)
(21) International Application Number: PCT/US89/04010 (22) International Filing Date: 15 September 1989 (15.09.89) (30) Priority data: 247,059 20 September 1988 (20.09.88) US (71) Applicant: RAYCHEM CORPORATION [US/US]; 300 Constitution Drive, Menlo Park, CA 94025 (US). (72) Inventors: SHAFE, Jeff ; 3323 Spring Street, Redwood City, CA 94063 (US). STRALEY, O., James ; 770 9th Avenue, Redwood City, CA 94063 (US). McCARTY, Gordon ; 2244 Belthorn Court, San Jose, CA 95131 (US). OSWAL, Ravinder, K. ; 4832 La Habra Street, Union City, CA 94587 (US). TRAMMELL, Bernadette, A. ; 7 Iris Lane, Menlo Park, CA 94025 (US).	(74) Agents: BURKARD, Herbert, G. et al.; Raychem Corporation, 300 Constitution Drive, Menlo Park, CA 94025 (US). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>	
(54) Title: CONDUCTIVE POLYMER COMPOSITION (57) Abstract <p>Electrical devices with improved resistance stability comprise a PTC element comprising a conductive polymer and two electrodes. The conductive polymer composition comprises an organic crystalline polymer and carbon black with a pH of less than 4.0. Particularly preferred conductive polymer compositions comprise carbon blacks which have a pH of less than 4.0, a dry resistivity R_{CB} and a particle size D in nanometers such that R_{CB}/D is at most 0.1. Electrical devices of the invention include heaters and circuit protection devices.</p>		

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CONDUCTIVE POLYMER COMPOSITION

BACKGROUND OF THE INVENTIONField of the Invention

This invention relates to conductive polymer compositions and electrical devices comprising them.

Background of the Invention

Conductive polymer compositions and electrical devices such as heaters and circuit protection devices comprising them are well-known. Reference may be made, for example, to U.S. Patent Nos. 3,793,716, 3,823,217, 3,858,144, 3,861,029, 3,914,363, 4,017,715, 4,177,376, 4,188,276, 4,237,441, 4,242,573, 4,246,468, 4,286,376, 4,304,987, 4,318,881, 4,330,703, 4,334,148, 4,334,351, 4,388,607, 4,400,614, 4,425,497, 4,426,339, 4,435,639, 4,459,473, 4,514,620, 4,520,417, 4,529,866, 4,534,889, 4,543,474, 4,545,926, 4,547,659, 4,560,498, 4,571,481, 4,574,188, 4,582,983, 4,631,392, 4,638,150, 4,654,511, 4,658,121, 4,659,913, 4,661,687, 4,667,194, 4,673,801, 4,698,583, 4,719,335, 4,722,758, and 4,761,541, European Patent Publication Nos. 38,718 (Fouts et al, published October 28, 1981), 158,410 (Batliwalla et al, published October 16, 1985), and 231,068 (Barma et al, published August 5, 1989).

Conductive polymer compositions which exhibit PTC (positive temperature coefficient of resistance) behavior are particularly useful for self-regulating strip heaters and circuit protection devices. These electrical devices utilize the PTC anomaly, i.e. an anomalous rapid increase in resistance as a function of temperature, to limit the

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heat output of a heater or the current flowing through a circuit. Compositions which exhibit PTC anomalies and comprise carbon black as the conductive filler have been disclosed in a number of references. U.S. Patent No. 4,237,441 (van Konynenburg et al.) discloses suitable carbon blacks for use in PTC compositions with resistivities less than 7 ohm-cm. U.S. Patent No. 4,388,607 (Toy et al) discloses appropriate carbon blacks for use in compositions for strip heaters. U.S. Patent No. 4,277,673 (Kelly) discloses self-regulating articles which comprise highly resistive carbon blacks. These blacks, either alone or in combination with a low resistivity carbon black, form PTC compositions which provide significantly shorter annealing times.

As indicated in the references, a large number of carbon blacks are suitable for use in conductive compositions. The choice of a particular carbon black is dictated by the physical and electrical properties of the carbon black and the desired properties, e.g. flexibility or conductivity, of the resulting composition. The properties of the carbon blacks are affected by such factors as the particle size, the surface area, and the structure, as well as the surface chemistry. This chemistry can be altered by heat or chemical treatment, either during the production of the carbon black or in a post-production process, e.g. by oxidation. Oxidized carbon blacks frequently have a low surface pH value, i.e. less than 5.0, and may have a relatively high volatile content. When compared to nonoxidized carbon blacks of similar particle size and structure, oxidized carbon blacks have higher resistivities. It is known that carbon blacks which are oxidized provide improved flow characteristics in printing inks, improved

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wettability in certain polymers, and improved reinforcement of rubbers.

SUMMARY OF THE INVENTION

We have now found that conductive polymer compositions with improved thermal stability can be made when the conductive filler comprises carbon black with a low pH. We have found that the use of such carbon blacks results in an increased PTC anomaly when compared to similar, nonoxidized carbon blacks, even when the composition is more highly reinforced due to an increased filler content required to compensate for higher resistivity. Therefore, in one aspect, this invention provides an electrical device which comprises

- (1) a PTC element comprising a conductive polymer composition which exhibits PTC behavior, which has a resistivity at 20°C R_{cp} , and which comprises
 - (a) an organic polymer which has a crystallinity of at least 5% and a melting point T_m , and
 - (b) carbon black which has a pH of less than 4.0; and
- (2) two electrodes which can be connected to a source of electrical power to pass current through the PTC element,

said electrical device having a resistance R_i at 20°C and being such that if the device is maintained at a temperature equal to T_m for a period of 50 hours and is then cooled to 20°C, its resistance at 20°C, R_{f50} , is from $0.25R_i$ to $1.75R_i$.

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We have found that the physical and electrical properties of the carbon black may be used to determine suitable fillers for use in compositions of the invention. Therefore, in a second aspect the invention provides a conductive polymer composition which exhibits PTC behavior and which comprises

- (1) an organic polymer which has a crystallinity of at least 5% and a melting point T_m , and
- (2) carbon black which has a pH of less than 4.0, a particle size of D nanometers and a dry resistivity R_{CB} such that (R_{CB}/D) is less than or equal to 0.1.

DETAILED DESCRIPTION OF THE INVENTION

The carbon blacks useful in the conductive polymer compositions of this invention have pH values of less than 5.0, preferably less than 4.0, particularly less than 3.0. The pH is a measure of the acidity or alkalinity of the carbon black surface. A pH of 7.0 indicates a chemically neutral surface; values less than 7.0 are acidic, those higher than 7.0 are basic. Low pH carbon blacks generally have a relatively high volatile content, volatile content being a measure of the amount of chemisorbed oxygen which is present on the surface of the carbon black. The amount of oxygen can be increased by oxidation in a post-production process. The resulting carbon black will have a higher surface activity. For purposes of this specification, the terms "low pH carbon black" and "oxidized carbon black" are used as equivalent terms. The pH of the carbon black is that which is measured prior to mixing the carbon black with the polymer.

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The low pH carbon blacks of this invention are used in conductive polymer compositions which exhibit PTC (positive temperature coefficient) behavior in the temperature range of interest when connected to a source of electrical power. The terms "PTC behavior" and "composition exhibiting PTC behavior" are used in this specification to denote a composition which has an R_{14} value of at least 2.5 or an R_{100} value of at least 10, and preferably both, and particularly one which has an R_{30} value of at least 6, where R_{14} is the ratio of the resistivities at the end and the beginning of a 14°C range, R_{100} is the ratio of the resistivities at the end and the beginning of a 100°C range, and R_{30} is the ratio of the resistivities at the end and the beginning of a 30°C range. In contrast, "ZTC behavior" is used to denote a composition which increases in resistivity by less than 6 times, preferably less than 2 times in any 30°C temperature range within the operating range of the heater.

Carbon blacks with suitable size, surface area and structure for use in PTC compositions are well-known. Guidelines for selecting such carbon blacks are found in U.S. Patent Nos. 4,237,441 (van Konynenburg et al.) and 4,388,607 (Toy et al.). In general, carbon blacks with a relatively large particle size, D (measured in nanometers), e.g. greater than 18 nm, and relatively high structure, e.g. greater than about 70 cc/100 g, are preferred for PTC compositions.

Carbon blacks which are particularly preferred for compositions of the invention are those which meet the criteria that the ratio of the resistivity of the carbon black (in powder form) to the particle size (in nanometers).

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is less than or equal to 0.1, preferably less than or equal to 0.09, particularly less than or equal to 0.08. The resistivity of the carbon black in ohm-cm is determined by following the procedure described in Columbian Chemicals Company bulletin "The Dry Resistivity of Carbon Blacks" (AD1078). In this test, 3 grams of carbon black are placed inside a glass tube between two brass plungers. A 5 kg weight is used to compact the carbon black. Both the height of the compacted carbon black and the resistance in ohms between the brass plunger electrodes are noted and the resistivity is calculated. The ratio is useful for carbons which are tested in their powder, not pelletized, form. While most nonoxidized carbon blacks fulfill the requirements of this ratio, the carbon blacks particularly useful in this invention are those which both meet the ratio and have a pH of less than 5.0.

Other conductive fillers may be used in combination with the designated carbon black. These fillers may comprise nonoxidized carbon black, graphite, metal, metal oxide, or any combination of these. When a nonoxidized carbon black, i.e. a carbon black with a pH of at least 5.0, is present, it is preferred that the pH of the nonoxidized carbon black be at least 1.0 pH unit greater than the pH of the oxidized carbon black. It is preferred that the low pH carbon black be present at a level of at least 5% by weight, preferably at least 10% by weight, particularly at least 20% by weight of the total conductive filler, e.g. 25 to 100% by weight of the total conductive filler. For most compositions of the invention, the low pH carbon black comprises at least 4% by weight, preferably at least 6% by weight, particularly at least 8% by weight of the total composition. For compositions which comprise inks, the presence of the

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solvent is neglected and the content of the solid components, e.g. carbon black and polymer, is considered the total composition.

Commercially available carbon blacks which have low pH values may be used. Alternatively, nonoxidized carbon blacks may be treated, e.g. by heat or appropriate oxidizing agents, to produce carbon blacks with appropriate surface chemistry.

The conductive polymer composition comprises an organic polymer which has a crystallinity of at least 5%, preferably at least 10%, particularly at least 15%, e.g. 20 to 30%. Suitable crystalline polymers include polymers of one or more olefins, particularly polyethylene; polyalkenamers such as polyoctenamer; copolymers of at least one olefin and at least one monomer copolymerisable therewith such as ethylene/acrylic acid, ethylene/ethyl acrylate, and ethylene/vinyl acetate copolymers; melt-shapeable fluoropolymers such as polyvinylidene fluoride, ethylene/tetrafluoroethylene copolymers, and terpolymers of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene; and blends of two or more such polymers. (The term "fluoropolymer" is used herein to denote a polymer which contains at least 10%, preferably at least 25%, by weight of fluorine, or a mixture of two or more such polymers.) In order to achieve specific physical or thermal properties for some applications, it may be desirable to blend one crystalline polymer with another polymer, either crystalline or amorphous. When there are two or more polymers in the composition, the blend must have a crystallinity of at least 5%. The crystallinity, as well as the melting point T_m are determined from a DSC (differential scanning calorimeter).

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trace on the conductive polymer composition. The T_m is defined as the temperature at the peak of the melting curve. If the composition comprises a blend of two or more polymers, T_m is defined as the lowest melting point measured for the composition (often corresponding to the melting point of the lowest melting component).

The composition may comprise additional components, e.g. inert fillers, antioxidants, flame retardants, prorads, stabilizers, dispersing agents. Mixing may be conducted by any suitable method, e.g. melt-processing, sintering, or solvent-blending. Solvent-blending is particularly preferred when the conductive polymer composition comprises a polymer thick film ink. The composition may be cross-linked by irradiation or chemical means.

The conductive polymer composition of the invention is used as part of a PTC element in an electrical device, e.g. a heater, a sensor, or a circuit protection device. The resistivity of the composition is dependent on the function of the electrical device, the dimensions of the PTC element, and the power source to be used. The resistivity may be, for example, from 0.01 to 100 ohm-cm for circuit protection devices which are powered at voltages from 15 to 600 volts, 10 to 1000 ohm-cm for heaters powered at 6 to 60 volts, or 1000 to 10,000 ohm-cm or higher for heaters powered at voltages of at least 110 volts. The PTC element may be of any shape to meet the requirements of the application. Circuit protection devices and laminar heaters frequently comprise laminar PTC elements, while strip heaters may be rectangular, elliptical, or dumbbell- ("dogbone"-) shaped. When the conductive polymer composition comprises an ink, the PTC element may be screen-printed or applied in any

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suitable configuration. Appropriate electrodes, suitable for connection to a source of electrical power, are selected depending on the shape of the PTC element. Electrodes may comprise metal wires or braid, e.g. for attachment to or embedment into the PTC element, or they may comprise metal sheet, metal mesh, conductive (e.g. metal- or carbon-filled) paint, or any other suitable material.

The electrical devices of the invention show improved stability under thermal aging and electrical stress. When a device is maintained at a temperature equal to T_m for a period of 50 hours, the resistance at 20°C measured after aging, i.e. R_{f50} , will differ from the initial resistance at 20°C, i.e. R_i , by no more than 75%, preferably no more than 60%, particularly no more than 50%, producing an R_{f50} of from 0.25 R_i to 1.75 R_i , preferably from 0.40 R_i to 1.60 R_i , particularly from 0.50 R_i to 1.50 R_i . If a similar test is conducted for 300 hours, the change in resistance will be less than 50%, preferably less than 40%, particularly less than 30%, producing a resistance at 20°C after 300 hours, R_{f300} , of from 0.50 R_i to 1.50 R_i , preferably from 0.60 R_i to 1.40 R_i , particularly from 0.70 R_i to 1.30 R_i . It is to be understood that if a device meets the resistance requirement when tested at a temperature greater than T_m , it will also meet the requirement when tested at T_m . Similar results will be observed when the device is actively powered by the application of voltage. The change in resistance may reflect an increase or decrease in device resistance. In some cases, the resistance will first decrease and then increase during the test, possibly reflecting a relaxation of mechanically-induced stresses followed by oxidation of the polymer. Particularly preferred compositions comprising fluoropolymers may exhibit stability which is better than a 30% change in resistance.

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The invention is illustrated by the following examples.

Examples 1 to 10

For each example, an ink was prepared by blending the designated percent by weight (of solids) of the appropriate carbon black with dimethyl formamide in a high shear mixer. The solution was then filtered and powdered Kynar[®] 9301 (a terpolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene with a melting point of about 88°C, available from Pennwalt) in an amount equal to (100 - % carbon black) was added to the filtrate and allowed to dissolve over a period of 24 to 72 hours. (Approximately 60% solvent and 40% solids was used in making the ink). Silver-based ink electrodes (Electrodag[®] 461SS, available from Acheson Colloids) were printed onto ethylene-tetrafluoroethylene substrates and samples of each ink were applied. Samples of each ink were aged in ovens at temperatures of 65, 85, 107 and 149°C. Periodically, the samples were removed from the oven and the resistance at room temperature (nominally 20°C), R_t , was measured. Normalized resistance, R_n , was determined by dividing R_t by the initial room temperature resistance, R_i . The extent of instability was determined by the difference between R_n and 1.00. Those inks which comprised carbon blacks with a pH of less than 5 were generally more stable than the inks comprising higher pH blacks.

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TABLE I

Stability of Conductive Inks After Aging
at Elevated Temperature for 300 Hours
(Resistance Measured at Room Temperature)

<u>Example/</u>	<u>Carbon</u> <u>Black</u>	<u>pH</u>	<u>Wt%</u> <u>CB</u>	<u>R_n @</u> <u>65°C</u>	<u>R_n @</u> <u>85°C</u>	<u>R_n @</u> <u>107°C</u>	<u>R_n @</u> <u>149°C</u>
1	Conductex™ SC	7.0	3.0	1.22	1.75	5.61	6.39
2	Raven™ 1500	6.0	3.0	1.01	1.92	11.88	20.0
3	Raven™ 890	6.5	6.0	1.27	1.77	2.92	6.07
4	Raven™ 850	7.0	4.0	1.32	2.05	4.08	8.48
5	Raven™ 1000	6.0	4.0	1.18	1.43	1.94	4.40
6	Raven™ 16	7.0	5.6	1.11	1.89	-	-
7	Raven™ 5750	2.1	8.1	0.87	0.92	0.97	0.56
8	Raven™ 1040	2.8	9.1	0.96	1.15	1.47	1.34
9	Raven™ 1255	2.5	6.0	1.04	1.26	1.12	0.65
10	Raven™ 14	3.0	7.0	0.82	1.00	-	-

Notes to Table I:

(1) Conductex and Raven are trademarks for carbon blacks available from Columbian Chemicals.

(2) Wt% CB indicates the percent by weight of carbon black used in each ink.

(3) Carbon blacks in Examples 1, 2 and 3 produced inks with ZTC characteristics.

Measurements on two samples at 93°C (i.e. $T_m + 5^\circ\text{C}$) showed that after 50 hours Example 6 (pH = 7.0) had an R_n of 2.53 and Example 10 (pH 3.0) had an R_n of 1.48.

The R_n values for Examples 1 to 6 and Examples 7 to 10 were averaged for each time interval at the test tem-

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peratures. The results, shown in Table II, indicate that the carbon blacks with high pH values were significantly less stable than those with low pH values.

TABLE IIAverage R_n Values

	<u>Hours @65°C</u>			<u>Hours @85°C</u>			<u>Hours @107°C</u>			<u>Hours @149°C</u>		
<u>Example</u>	<u>300</u>	<u>675</u>	<u>1256</u>	<u>300</u>	<u>675</u>	<u>1256</u>	<u>300</u>	<u>675</u>	<u>1256</u>	<u>300</u>	<u>675</u>	<u>1256</u>
1 to 6 (pH>5)	1.2	1.2	1.2	1.8	1.8	1.9	5.3	7.9	9.0	9.1	14.2	15.6
7 to 10 (pH<5)	0.9	0.9	0.9	1.1	1.0	1.0	1.2	1.3	1.3	0.9	1.0	1.0

Additional tests were conducted on samples from Examples 6 and 10 in order to determine the stability of the compositions under applied voltage. After measuring the initial room temperature resistance, the samples were placed in environmental chambers maintained at either 20 or 65°C and appropriate voltage was applied to each sample in order to produce comparable watt densities. Periodically, the voltage was disconnected and the resistance of each sample measured. R_n was calculated as previously described. It is apparent from the results in Table III that the samples containing the oxidized carbon black were more stable than those with nonoxidized carbon black.

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TABLE III

R_n of Samples After Active Testing
(Time in Hours)

	<u>pH</u>	<u>Applied Volts</u>	<u>Power (w/in²)</u>		<u>R_n 20°C</u>				<u>R_n 65°C</u>			
			<u>Samples at</u>		<u>300</u>	<u>600</u>	<u>1000</u>	<u>4000</u>	<u>300</u>	<u>600</u>	<u>1000</u>	<u>4000</u>
			<u>20°C</u>	<u>65°C</u>								
Example 6												
Raven [™] 16	7.0	120	2.3	2.8	1.1	1.3	1.5	6.0	1.4	1.5	1.5	2.0
Example 10												
Raven [™] 14	3.0	240	1.9	3.1	0.8	0.8	0.8	0.7	0.9	0.8	0.7	0.8

Examples 11 to 14

Following the procedure of Examples 1 to 10, inks were prepared using Kynar[™] 9301 as a binder and incorporating the carbon blacks listed in Table IV. The resistance vs. temperature characteristics were measured by exposing samples of each ink to a temperature cycle from 20°C to 82°C. The height of the PTC anomaly was determined by dividing the resistance at 82°C (R_{82}) by the resistance at 20°C (R_{20}). It was apparent that at comparable resistivity values the PTC anomaly was higher for the oxidized carbon blacks than for the nonoxidized carbon blacks.

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TABLE IV

<u>Carbon</u> <u>Example/Black</u>	<u>pH</u>	<u>D</u> <u>(nm)</u>	<u>S.A.</u> <u>(m²/g)</u>	<u>DBP</u> <u>(cc/100g)</u>	<u>R_{CB}</u> <u>(ohm-cm)</u>	<u>R_{CB}/D</u>	<u>Wt%</u>	<u>Rho</u> <u>(ohm-cm)</u>	<u>PTC</u> <u>Height</u>
11 Raven [®] 1000	6.0	28	95	63	2.46	0.088	4.0	750	3.1x
12 Raven [®] 1040	2.8	28	90	99	19.20	0.695	9.1	720	13.0x
13 Raven [®] 450	8.0	62	33	67	1.36	0.021	5.0	150	23x
14 Raven [®] 14	3.0	59	45	111	4.36	0.074	12.0	100	42x

Notes to Table IV:

- (1) D represents the particle size of the carbon black in nm.
- (2) S.A. represents the surface area of the carbon black in m²/g as measured by a BET nitrogen test.
- (3) DBP is a measure of the structure of the carbon black and is determined by measuring the amount in cubic centimeters of dibutyl phthalate absorbed by 100 g of carbon black.
- (4) Wt% represents the percent by weight of the total solids content of the ink that is carbon black.
- (5) Rho is the resistivity of the ink in ohm-cm.
- (6) PTC Height is the height of the PTC anomaly as determined by R_{g2}/R₂₀.
- (7) R_{CB} is the dry resistivity of the carbon black in powder form under a 5 kg load.

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- (8) $R_{CB/D}$ is the ratio of the dry resistivity of the carbon black to the particle size.

Example 15

Using a Brabender™ mixer, 85% by weight of Kynar™ 9301 was melt-processed with 15% by weight of Raven™ 16. (Raven™ 16 has a pH of 7.0, a particle size of 61 nm, a surface area of 25 m²/g, a DBP of 105 cc/100 g and a dry resistivity of 1.92.) The compound was pelletized and then extruded through a strand die to produce a fiber with a diameter of approximately 0.070 inch (0.18 cm). Silver paint (Electrodag™ 504 available from Acheson Colloids) was used to apply electrodes to pieces of the fiber. The fiber pieces were then tested at 85°C, 107°C, and 149°C following the procedure of Examples 1 to 10. The results are shown in Table V. The test for these samples was discontinued after 743 hours.

Example 16

Following the procedure of Example 15, 20% by weight of Raven™ 14 was mixed with Kynar™ 9301, extruded into a fiber, and thermally aged. The results as shown in Table V indicate that this oxidized carbon black was more stable on aging than a similar carbon black with a higher pH. When tested at 93°C, i.e. ($T_m + 5$)°C, fibers of Example 15 had an R_n after 50 hours of 2.76; those of Example 16 had an R_n of 1.73.

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TABLE V R_n Values for Extruded Fibers

	Time in Hours					
	<u>146</u>	<u>265</u>	<u>743</u>	<u>1058</u>	<u>1687</u>	<u>2566</u>
85°C:						
Ex.15 (Raven [™] 16)	2.61	3.13	3.12	-	-	-
Ex.16 (Raven [™] 14)	1.40	1.23	1.05	1.15	1.15	1.16
107°C:						
Ex. 15 (Raven [™] 16)	3.95	4.40	101	-	-	-
Ex. 16 (Raven [™] 14)	0.78	0.98	1.12	0.80	1.16	1.05
149°C:						
Ex. 15 (Raven [™] 16)	27.6	137	604	-	-	-
Ex. 16 (Raven [™] 14)	0.65	1.07	1.52	1.43	1.91	2.83

Example 17

Following the procedure of Example 15, fibers were prepared by blending 55% by weight Elvax[™] 250 (ethylene vinyl acetate copolymer with a melting point of 60°C, available from Dow) and 45% by weight Raven[™] 22 (carbon black with a pH of 7.0, a particle size of 62 nm, a surface area of 25 m²/g, and a DBP of 113 cc/100 g, available from Columbian Chemicals). An ink was prepared by dissolving the fibers in xylene. After 813 hours at 52°C, the R_n value was 0.94.

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Example 18

Following the procedure of Example 17, fibers were first prepared with 50% by weight Raven[™] 14 in Elvax[™] 250 and were then dissolved in xylene. After 813 hours at 52°C, the R_n value of the ink was 0.88.

Example 19

Fibers were prepared from 76% by weight PFA[™] 340 (a copolymer of tetrafluoroethylene and a perfluorovinyl ether with a T_m of 307°C, available from du Pont) and 24% by weight Raven[™] 600 (carbon black with a pH of 8.3, particle size of 65 nm, DBP of 82 cc/100g, and surface area of 34 m²/g, available from Columbian Chemicals) as in Example 15. Samples tested at 311°C for 50 hours had an R_n of 0.55.

Example 20

Following the procedure of Example 19, fibers were prepared with 17% by weight Raven[™] 14. After 50 hours at 311°C, the R_n value was 0.93.

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What is claimed is:

1. An electrical device which comprises

(1) a PTC element comprising a conductive polymer composition which exhibits PTC behavior, which has a resistivity at 20°C, R_{cp} , and which comprises

(a) an organic polymer which has a crystallinity of at least 5% and a melting point T_m , and

(b) carbon black which has a pH of less than 4.0; and

(2) two electrodes which can be connected to a source of electrical power to pass current through the PTC element,

said electrical device having a resistance R_i at 20°C and being such that if the device is maintained at a temperature equal to T_m for a period of 50 hours and is then cooled to 20°C, its resistance at 20°C, R_{f50} , is from $0.25R_i$ to $1.75R_i$.

2. An electrical device according to claim 1 wherein the device is such that if the device is maintained at a temperature equal to T_m for a period of 300 hours and is then cooled to 20°C, its resistance at 20°C, R_{f300} , is from $0.5R_i$ to $1.5R_i$.

3. An electrical device according to claim 1 or 2 wherein the carbon black has a pH of less than 3.0.

4. An electrical device according to claim 1, 2, or 3 wherein the conductive polymer comprises a polymer thick film ink.

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5. An electrical device according to any one of the preceding claims wherein the electrical device comprises a heater or a circuit protection device.

6. An electrical device according to any one of the preceding claims wherein the conductive polymer has been crosslinked.

7. An electrical device according to any one of the preceding claims wherein the carbon black is present at at least 4% by weight.

8. An electrical device according to any one of the preceding claims wherein the composition further comprises (1) carbon black which has a pH which is at least 5.0 or (2) graphite.

9. An electrical device according to any one of the preceding claims wherein the polymer is a fluoropolymer.

10. An electrical device according to any one of the preceding claims wherein the carbon black has a particle size of D nanometers and a dry resistivity R_{CB} such that (R_{CB}/D) is less than or equal to 0.1.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/04010

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : H 01 C 7/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC ⁵	H 01 C	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT*		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
X	US; A, 4277673 (KELLY) 7 July 1981 see column 2, lines 20-28; column 5, lines 14-59 cited in the application	1,3,5,7-9
A	US, A, 4237441 (VAN KONIJNENBURG et al.) 2 December 1980 see column 1, lines 61-68; column 2, lines 25-35; column 4, lines 42-49; column 5, line 59 - column 6, line 37 cited in the application	1,5-7,9,10
A	EP, A, 0123540 (RAYCHEM CORPORATION) 31 October 1984 see page 2, line 24 - page 3, line 16; page 4, lines 21-30; page 5, lines 23-26; page 6, lines 10-14	1,5,7,8
A	US, A, 4591700 (SOPORY) 27 May 1986 see claim 1	1,5,9
<p>* Special categories of cited documents: **</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
1st December 1989	08 JAN. 1990	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	T.K. WILLIS	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	EP, A, 0235454 (SUNBEAM CORPORATION) 9 September 1987 see page 2, lines 9-22, 46-48; page 6, lines 21-30	1,6-8
A	US, A, 4668857 (SMUCKLER) 26 May 1987 see column 4, lines 36-41; claims 1,4,6 -----	1,5,9

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8904010
SA 31305

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 22/12/89
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU-A- 5685080	02-10-80
		CA-A- 1136846	07-12-82
		DE-A,C 3011754	09-10-80
		DE-C- 3050761	05-06-85
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		GB-A,B 2036754	02-07-80
		JP-A- 55078406	13-06-80
EP-A- 0123540	31-10-84	JP-A- 59206441	22-11-84
US-A- 4591700	27-05-86	None.	
EP-A- 0235454	09-09-87	AU-A- 6588486	11-06-87
		JP-A- 62155502	10-07-87
US-A- 4668857	26-05-87	None	

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